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Correlations of Hydrogen Chloride and Hydrogen Cyanide Concentrations Evolved During Combustion of Chlorine- and Nitrogen-Containing Materials

By Maria I. De Rosa

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

U.S. Department of the Interior
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Report of Investigations 9521

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UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mL	milliliter
g	gram	p/cm^3	particle per cubic centimeter
g/g	gram per gram	p/g	particle per gram
g/s	gram per second	pct	percent
L	liter	ppm	part per million
L/min	liter per minute	s	second
m^3/s	cubic meter per second	μm	micrometer
mg/g	milligram per gram	°C	degree Celsius
min	minute		

CORRELATIONS OF HYDROGEN CHLORIDE AND HYDROGEN CYANIDE CONCENTRATIONS EVOLVED DURING COMBUSTION OF CHLORINE- AND NITROGEN-CONTAINING MATERIALS

By Maria I. De Rosa[1]

ABSTRACT

The U.S. Bureau of Mines conducted a study to determine if correlations exist between the chlorine or nitrogen contents of materials and the hydrogen chloride (HCl) or hydrogen cyanide (HCN) concentrations evolved during the thermal decomposition of these materials. Hydrogen chloride, hydrogen cyanide, and carbon monoxide (CO) were found to be the primary toxic gases evolved during the combustion process.

The experiments were carried out in a 20-L furnace with 1-g samples. The furnace temperature, rising from ambient, was set at 1,000 °C with an airflow of 10 L/min. The variables measured were the gas loads (milligrams per gram) of HCl, HCN, CO, and CO_2 (carbon dioxide); CO and CO_2 concentrations as a function of time were also measured.

Other variables included the average concentrations of submicrometer smoke particles and particles' average diameter, mass of particulates, sample and furnace temperatures, and sample weight loss.

The data indicate that there are significant correlations between the percentage of chlorine or nitrogen contained in the original samples and the HCl or HCN concentrations evolved during the combustion of the materials. These correlations may be used to predict and evaluate a material's toxic hazard during combustion.

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INTRODUCTION

Within the mine health and safety program, the U.S. Bureau of Mines (USBM) continues its studies of belt materials' properties during combustion to prevent mine fires and fire fatalities. The atmosphere produced by a fire is a dynamic, rapidly changing combination of toxic gases, particulates, reduced oxygen (O_2), and high temperatures. In this atmosphere, visibility is generally low. Each component of this combination is capable of producing conditions that are incompatible with human life. As statistics (*1*)[2] have shown, the majority of fire fatalities results from smoke inhalation, prolonged by the inability to escape because of poor or nonexistent visibility, and not from burns. Therefore, the identification of the hazardous combustion products, evolved from materials under different fire conditions and times, is important.

During a fire, irritant [hydrogen chloride (HCl)] and asphyxiant [hydrogen cyanide (HCN) and carbon monoxide (CO)] gases may be present. Irritant gases produce sensory irritation of the eyes and of the upper respiratory tract, and pulmonary irritation. Most irritants produce signs and symptoms characteristic of both sensory and pulmonary irritation (*2-3*).

Hydrogen chloride gas concentrations of 100 ppm are immediately dangerous to life and health (IDLH). At this concentration, a breathing apparatus must be used; in case of apparatus failure, a person may escape within 30 min without ill effects (*4*). The gas has been implicated as the principal contributor to the overall toxicity during the thermal decomposition of polyvinyl chloride (PVC) materials. Other gases and/or aerosols evolved have been found to contribute only to a small extent to the overall toxicity (*5*).

Exposure to HCl causes impairments of the respiratory function and morphological injury, both in the upper airways and in the alveolar region (*6-7*). Studies on the evaluation of human performance, in terms of distance and time traveled, under atmospheres containing HCl, CO, and low O_2 concentrations, have shown deterioration of performance (*8*). Hydrogen chloride and carbon monoxide gases have been found to act in an additive manner (*9*). Also, animal studies have shown that the time and concentration values of HCl that cause incapacitation are not significantly different from those causing death (*9*).

Hydrogen cyanide (IDLH value, 50 ppm), which evolves from the combustion of nitrogen-containing materials, is a very rapidly acting toxicant whose action inhibits the utilization of O_2 by cells (*10*). The effects of the asphyxiant increase in severity with increasing doses and exposure time (*11-14*). Furthermore, in a fire in which a person is first intoxicated by HCN, the subsequent release of CO may produce both sublethal and lethal concentrations of CO in the blood (*15*). Hydrogen cyanide and carbon monoxide gases have been found to act in an additive manner (*16*).

Finally, CO (IDLH value, 1,500 ppm), which evolves from the combustion of all organic materials, shows great affinity for the hemoglobin in the blood. Even partial conversion of hemoglobin to carboxyhemoglobin (COHb) reduces the O_2-transport capability of the blood and results in a decreased supply of O_2 to body tissues (*17-19*). Carbon monoxide concentrations of 70, 100, 300, 500, and 900 ppm cause, respectively, COHb saturations of approximately 11, 14, 33, 45, and 60 pct. The increase in COHb of 9.1, 16, 20, 40, and 50 pct saturation produces, respectively, frontal headache, abnormal response, nausea, severe headache, and coma (*20-21*).

Previous USBM studies (*22-29*) have shown that HCl and HCN gases evolve during the combustion of materials containing chlorine and nitrogen; many of these materials are found in underground mines. In this study, the USBM set out to determine if correlations exist between the HCl and HCN concentrations (treated as load values) in combustion products and the percentage of chlorine and nitrogen contained in the original samples. These gases, together with CO, have been found to be the primary gas toxicities evolved during the combustion of these types of materials (*6, 14*). These correlations may be used to evaluate and predict the potential toxic hazard of chlorine- and nitrogen-containing materials during a fire. Also, the quantification of CO, CO_2 (carbon dioxide), submicrometer smoke particles [on whose surfaces gases adhere and whereby the toxic agents are carried deeper into the lower respiratory tract (*30-32*)], and mass of particulates [which lodge with their carcinogenic agents into the respiratory and digestive tracts (*33*)] can contribute to the evaluation of a material's toxic hazard.

BACKGROUND

When a material undergoes combustion, a complex mixture of airborne solid and liquid particulates, and gases is evolved. In all fires, combustion is maintained by the reaction of the O_2 in the air with combustible gases, produced from the thermal decomposition of burning materials. During the process, heat, ash, and light are

[2]Italic numbers in parentheses refer to items in the list of references at the end of this report.

released. Many common materials, both natural and synthetic, contain halogens, nitrogen, sulfur, carbon, and hydrogen. When these materials are burned, HCl, HCN, HF (hydrogen fluoride), HBr (hydrogen bromide), CO, NO_x (oxides of nitrogen), SO_2 (sulfur dioxide), and NH_3 (ammonia) are formed (*34*).

Analyses of real-fire atmospheres have been conducted using portable smoke-sampling devices. The results of these analyses confirm that combustion products are produced in sufficient concentrations to create toxicologically hazardous environments (*35-36*).

Mounting concern over the contribution of materials to the hazards of smoke has resulted in an accelerated development of the science of combustion toxicology. Problems arise when the toxicities of mixtures of particulates and gases, whose compositions change as rapidly as the combustion process and ambient conditions, have not yet been identified.

At the present time, the standard methods used to assess the smoke toxicities of materials are bioassay methods, supplemented with analyses of primary toxic gas concentrations (*37*). In the bioassay methods, the toxicity of the smoke is evaluated on the basis of laboratory animals' response (lethality and/or incapacitation) to the smoke. The time and concentrations of primary toxic gases, at which death and/or incapacitation occur, and the amount of material that yields those concentrations differentiate one material from another. It derives that each material needs to be evaluated by bioassay method even if its content does not vary from a previously tested material because of the lack of correlations between the primary toxic gases evolved during the combustion of materials and the chemical contents of those materials. This methodology leads to unnecessary and expensive experimental-analytical repetitions.

The intent of this study is to simplify the process by classifying materials according to the prevalent chemical content in the original sample and by correlating the percentage of the material's chemical content with the primary toxic gas concentrations evolved during the combustion of these materials. Therefore, materials falling in the same class may be ranked simply and inexpensively, both according to the percentage of their chemical contents and according to the primary toxic gas concentrations evolved during the combustion of those contents.

EXPERIMENTAL SYSTEM

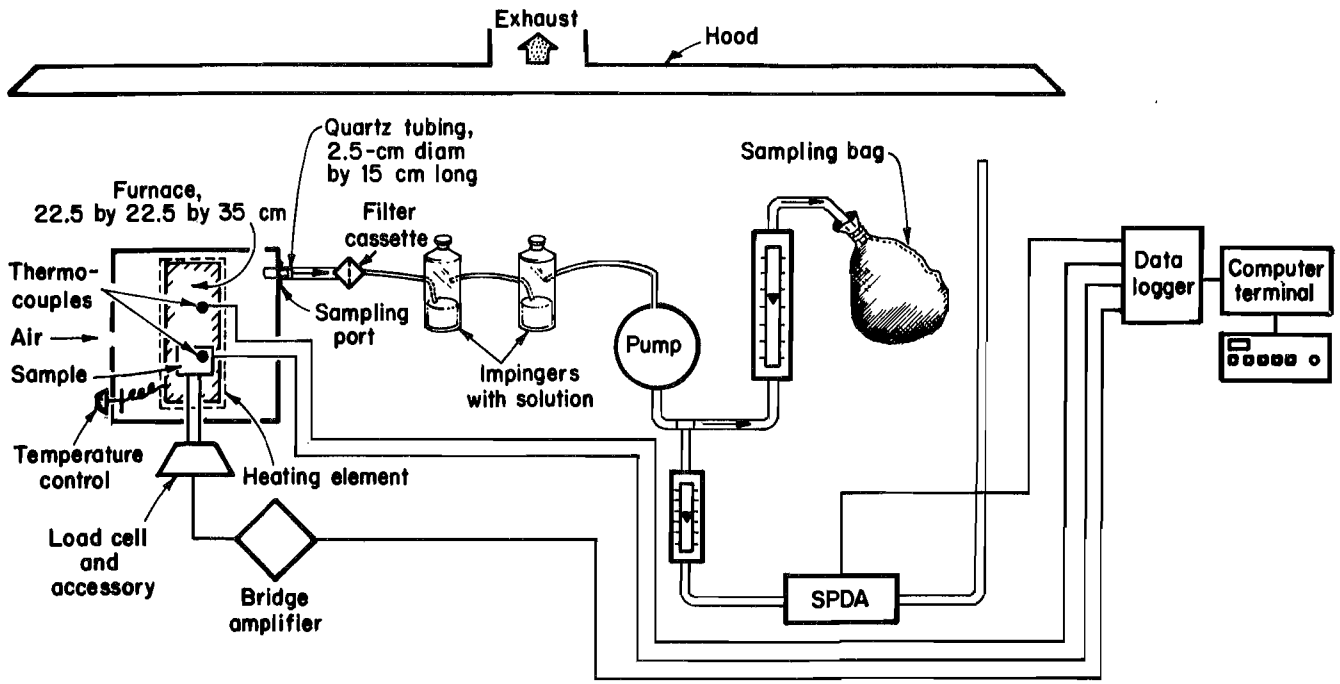
The experimental system (figure 1) consists of a 20-L furnace whose temperature rises from ambient at a rate that depends on the set temperature. In the experiments described herein, the furnace, set at 1,000 °C, reached a maximum temperature of 620 °C at the 20th minute (figure 2). A load cell, located under the furnace floor, contacts a quartz sample-cup (2.5-cm-diam) pedestal via an opening at the center of the furnace floor and transmits the sample weight loss (voltages) via a bridge amplifier to a data acquisition system. The total sample weight loss is also verified by sample weighing. The sample and furnace temperatures (monitored by thermocouples), and the output (voltages) of the submicrometer smoke particle detector analyzer (SPDA) (*38*), which measures the average submicrometer smoke particle concentration (n_σ), and particles' average diameter (d_g) are also transmitted to the data acquisition system. The data, logged in 10-s intervals, are mathematically treated, displayed, and printed by means of a miniframe computer via a laboratory-based real-time data acquisition system.

During the experiments, an exhaust pump draws ambient air, at a constant rate of 10 L/min, into the furnace (via an opening at the center of the furnace door) for a 20-min duration. This duration was chosen because all the samples, with exception of the fiberglass brattice (F1) (containing 90 pct of inorganic materials), underwent complete thermal decomposition during this time; only ash-like residues remained.

During one set of experiments, the combustion air is directed through a quartz tube located in the upper back of the furnace into a filter-cassette. The filter is connected to two consecutive impingers, each containing 15 mL of sodium or potassium hydroxide gas-trapping solutions (0.01 pct), to recover the HCl or the HCN in the gaseous forms, respectively. During a second set of experiments (no filters and no impingers are used), some of the combustion air is directed into the SPDA; the remaining combustion air is directed into a plastic sampling bag.

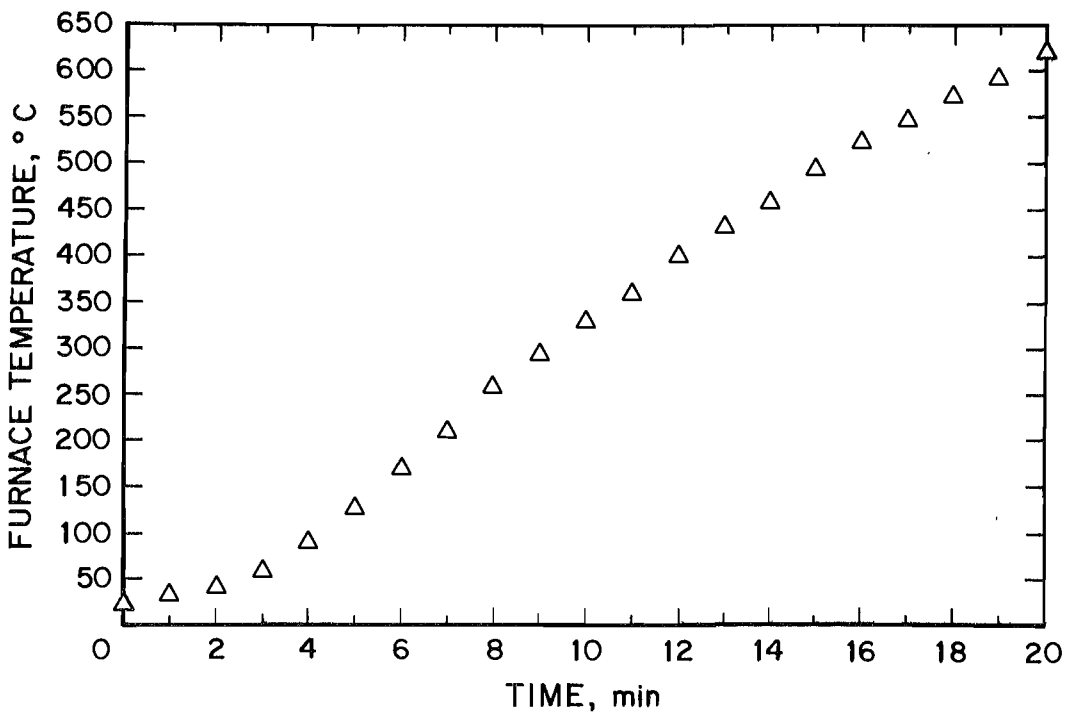
The directing of the combustion air into the filter-cassette (first set of experiments) and into the SPDA (second set of experiments) begins at a sample temperature of approximately 150 °C (no appreciable gas concentrations evolve at lower temperatures); with the present system, this temperature is reached at about the seventh minute into the experiment. Also, syringe grab samples of combustion air are taken from the sampling port at 1-min intervals and from the sampling bag at the end of each experiment.

Figure 1



Experimental system (20-L furnace).

Figure 2



Furnace temperature versus time at 1,000 °C set furnace temperature.

EXPERIMENTAL PROCEDURE AND DATA REDUCTION

CHLORINE-CONTAINING MATERIALS

Two sets of experiments with five different samples (five experiments in each set) were performed at a set furnace temperature of 1,000 °C. The experiments were repeated to verify the results; because the data were similar, this study only reports the values measured in the original experiments.

The samples underwent various stages of combustion from smoldering through flaming and ashing. The materials used were 1-g samples of PVC (P1), neoprene (N1), and styrene-butadiene rubber (SBR) (S1) mine conveyor belts; also used were 1-g samples of PVC (B1) and fiberglass (F1) mine brattices. A description and analysis of the materials are reported in table 1. The chlorine content of the materials was determined by the American Society for Testing and Materials (ASTM) test method D4208.

Table 1.—Description and analyses of materials

Materials	Description	Chlorine or nitrogen, pct
	CHLORINE-CONTAINING	
Conveyor belt:		
P1	Derived from PVC polymer; fillers have been added.	23
N1	Derived from neoprene rubber polymer; fillers have been added.	11
S1	Derived from SBR polymer; untreated for fire retardancy.	0.1
Brattice:		
B1	Derived from PVC polymer; fillers have been added.	28
F1	Fiberglass (>90 pct) fibers; treated with chlorinated additives for fire retardancy.	5
	NITROGEN-CONTAINING	
Flexible polyurethane foam:		
Pr	Derived from toluene diisocyanate; treated with chlorinated additives for fire retardancy.	4.79
Pn	Derived from toluene diisocyanate; untreated for fire retardancy.	4.78
Ny	Derived from polymerization of amino acid; untreated for fire retardancy.	11.46
Wl	Wool tinted fabric; untreated for fire retardancy.	13.25
Cb	Derived from natural fiber; treated with chlorinated additives for fire retardancy.	0.24

During the first set of experiments, the combustion air was directed into a filter cassette to recover the HCl attached to smoke particles (aerosol form), and the mass of smoke particulates. The HCl concentrations (recovered by the U.S. Environmental Protection Agency (EPA), test method 26) were analyzed by ion chromatography (National Institute for Occupational Safety and Health (NIOSH), test method 7903 for hydrochloric acid). The HCl aerosol and gaseous concentrations yielded the HCl load values (milligrams per gram or grams per gram of initial sample). Equation 1 converts the HCl load values to parts per million in a ventilated system:

$$\text{ppm HCl} = \frac{Y_{HCl} \times \dot{M}_s}{Q \times C_{HCl}}, \qquad (1)$$

where Y_{HCl} = load value of HCl, g/g,

$\dot{M}_s$ = sample mass loss rate, g/s,

Q = volumetric airflow, m^3/s,

and C_{HCl} = conversion constant (1.63×10^{-3}, $\frac{g}{m^3 \times ppm}$).

In the ventilated system used herein, the mass loss rate is the average mass loss occurring during approximately 600 s; no appreciable mass loss occurs before the 10th minute. The mass of smoke particulates was also treated as load value (milligrams per gram of initial sample).

During the second set of experiments, some of the combustion air (1.6 L/min) was directed into the SPDA and the remaining combustion air was directed into a sampling bag. The combustion air directed into the SPDA was used to measure the n_o (particles per cubic centimeter) and the d_g (micrometers). The sum of n_o, multiplied by a factor of 6.25 (because the airflow exhausted through the SPDA is 6.25 times less than the airflow exhausted through the furnace), yielded the n_o load values (particles per gram). The smoke particle characteristics, n_o and d_g, were derived as discussed in previous reports (*22-29*).

Syringe grab samples of combustion air taken at 1-min interval from the sampling port, were analyzed for concentrations of CO (parts per million) and CO_2 (parts per million) by gas chromatography. Syringe grab samples from the sampling bag were analyzed by gas chromatography for concentrations (treated as load values) of CO (milligrams per gram) and CO_2 (milligrams per

gram). The CO load values were normalized to HCl values, by dividing each CO value by a factor of 15 (CO IDLH value = 1,500 ppm; HCl IDLH value = 100 ppm) because CO is at least 15 times less toxic than HCl, and combined with the HCl load values (combined load, milligrams per gram). Other variables measured were the sample and furnace temperatures (degrees Celsius), and sample weight loss (grams). Only the total weight loss values are reported in this study.

NITROGEN-CONTAINING MATERIALS

Two sets of experiments with five different samples (five experiments in each set) were performed at a set furnace temperature of 1,000 °C. The experiments were repeated to verify the results, and the data are reported in the same manner described for the chlorine-containing materials. The samples used were 1-g of flexible polyurethane foams treated (Pr) and untreated (Pn) for flame retardancy, nylon (Ny) and wool (Wl) fabrics, and cotton batting (Cb) treated for flame retardancy. A description and analysis of the materials are reported in table 1. The nitrogen content of the materials was determined by the ASTM test method D3179.

During the first set of experiments, the combustion air was directed into a filter cassette to recover the HCN attached to smoke particles (aerosol form) and the mass of smoke particulates, and into solution-containing impingers, as described above. The HCN concentrations were analyzed by ion chromatography (NIOSH test method 7905 for cyanide).

The HCN aerosol and gaseous concentrations yielded the HCN load (milligrams per gram or grams per gram of initial sample). Equation 2 converts the HCN load values to parts per million in a ventilated system:

$$\text{ppm HCN} = \frac{Y_{HCN} \times \dot{M}_s}{Q \times C_{HCN}}, \qquad (2)$$

where Y_{HCN} = load value of HCN, g/g,

and C_{HCN} = conversion constant (1.21×10^{-3}, $\frac{g}{m^3 \times ppm}$).

The mass loss rate may be derived in the same manner as described for the chlorine-containing materials. The mass of smoke particulates was treated as load value (milligrams per gram of initial sample).

During the second set of experiments, some of the combustion air (1.6 L/min) was directed into the SPDA to measure the smoke particle characteristics, n_o and d_g. The remaining combustion air was directed into a sampling bag. Syringe grab samples of combustion air taken from the sampling port and sampling bag were analyzed for CO and CO_2 by gas chromatography and treated in the same manner reported in the procedures for chlorine-containing materials.

The CO load values were normalized to HCN values, by dividing each CO load value by a factor of 30 (CO IDLH value = 1,500 ppm; HCN IDLH value = 50 ppm) because CO is at least 30 times less toxic than HCN, and combined with the HCN load values (combined load, milligrams per gram of initial sample). Other variables measured were the sample and furnace temperatures (degree Celsius), and sample weight loss (grams). Only the total weight loss values are reported in this study.

RESULTS AND DISCUSSION

CHLORINE-CONTAINING MATERIALS

All the samples, with the exception of F1, which contained 90 pct glass fibers, underwent complete thermal decomposition (table 2). Only friable ash-like residues remained. The B1 sample, followed by the P1 and N1 samples, released the highest HCl concentrations and yielded the highest HCl loads (table 3) because of the high chlorine content of the materials. The concentrations were mostly in the gaseous form, although measurable aerosol concentrations were also found.

The HCl load values were correlated with the percentage of chlorine contained in the original sample (figure 3) using a least squares regression analysis.

The fit, reported in equation 3, was found to be:

$$Y_{HCl}\ (g/g) = 0.00105 \times Cl_2\ (pct) + 0.000315. \qquad (3)$$

The correlation coefficient (r^2) = 0.889; the standard deviation = 1.05.

The validity of the correlation may be increased by testing a larger number of materials with various chlorine contents. The present data, however, indicate that a direct and significant relationship exists between the two parameters. The higher the chlorine content, the higher the HCl load.

Also, the P1 and B1 samples, followed by the N1 sample, released high concentrations and loads of CO and CO_2, high concentrations and loads of submicrometer smoke particles (with the smallest diameter), and mass of particulates (tables 2 and 3, and figure 4). The CO load values, normalized to and combined with the HCl load values, increased the toxicity of these materials (table 3).

Table 2.—Oxidative thermal decomposition data for chlorine-containing materials at 1,000 °C set furnace temperature

Material[1]	Time, min	CO, ppm	CO_2, ppm	Temp, °C		n_o, 10^6 p/cm^3	d_g, μm	Total weight loss, g
				Sample	Furnace			
P1	6	15	500	92	160	10	<0.01	
	7	20	500	128	206	62	<0.01	
	8	39	500	169	250	109	<0.01	
	9	42	500	213	291	110	<0.01	
	10	58	600	254	329	2	0.11	
	11	157	600	291	367	21	0.06	
	12	431	800	336	403	4	0.27	0.85
	13	965	1,300	382	438	8	0.08	
	14	1,560	2,300	438	472	37	0.04	
	15	1,870	3,600	489	505	34	0.04	
	16	1,010	6,800	541	542	20	0.02	
	17	568	3,000	589	570	15	0.01	
	18	502	2,500	628	597	8	0.01	
	19	304	1,900	600	610	5	0.01	
	20	175	1,000	580	620	3	0.01	
N1	6	16	500	111	157	0	NAp	
	7	25	500	149	203	0	NAp	
	8	28	500	190	247	15	<0.01	
	9	35	500	231	289	9	<0.01	
	10	42	500	273	328	62	<0.01	
	11	127	700	320	366	32	0.01	
	12	473	800	381	402	40	0.02	0.75
	13	670	1,100	422	437	59	0.02	
	14	1,111	1,900	464	472	50	0.02	
	15	1,490	3,600	516	505	35	0.02	
	16	771	3,400	575	535	21	0.02	
	17	510	3,100	617	564	19	0.02	
	18	453	3,200	651	591	19	0.02	
	19	300	2,500	601	600	10	0.01	
	20	150	1,800	585	619	5	0.01	
S1	6	10	400	105	160	0	NAp	
	7	20	400	142	205	0	NAp	
	8	39	400	183	249	3	<0.01	
	9	50	400	228	290	9	<0.01	
	10	58	400	279	379	5	0.04	
	11	87	400	310	366	10	0.07	
	12	245	500	342	402	32	0.04	0.80
	13	1,270	17,600	390	436	67	0.03	
	14	404	17,500	467	481	98	0.01	
	15	203	10,900	520	517	5	0.05	
	16	235	2,700	544	542	15	<0.01	
	17	274	2,600	578	568	20	<0.01	
	18	316	2,500	605	593	3	0.03	
	19	200	1,500	590	600	2	0.02	
	20	105	1,002	550	615	1	0.01	
B1	6	14	600	107	172	0	NAp	
	7	14	600	142	218	0	NAp	
	8	19	600	184	261	1	0.05	
	9	30	600	218	301	1	0.38	
	10	103	700	238	340	2	0.30	
	11	336	900	269	378	41	0.05	
	12	822	900	314	414	182	0.02	0.96
	13	1,310	1,200	384	449	62	0.04	
	14	1,290	1,600	470	483	383	0.03	
	15	1,450	2,400	520	515	441	0.01	
	16	785	2,600	561	545	29	0.06	
	17	581	2,200	604	572	2	0.12	
	18	541	2,100	637	599	0.3	0.15	
	19	320	1,500	600	610	0.20	0.10	
	20	190	1,100	580	621	0.10	0.10	

See explanatory notes at end of table.

Table 2.—Oxidative thermal decomposition data for chlorine-containing materials at 1,000 °C set furnace temperature—Continued

Material[1]	Time, min	CO, ppm	CO_2, ppm	Temp, °C		n_o, 10^6 p/cm^3	d_g, μm	Total weight loss, g
				Sample	Furnace			
F1	6	14	500	106	163	0	NAp	
	7	19	500	144	208	0	NAp	
	8	25	500	186	252	0.01	0.33	
	9	38	500	231	293	0.07	0.68	
	10	87	500	276	333	0.15	0.93	
	11	187	600	323	371	0.45	0.38	
	12	213	700	370	407	0.11	0.27	0.2
	13	211	900	417	442	0.66	0.64	
	14	64	700	459	476	0.01	0.47	
	15	77	800	492	507	0	NAp	
	16	189	1,200	521	537	0	NAp	
	17	261	2,400	550	566	0	NAp	
	18	100	1,500	579	593	0	NAp	
	19	50	1,000	550	600	0	NAp	
	20	25	700	500	617	0	NAp	

d_g Average diameter of submicrometer smoke particles.
n_o Average concentration of submicrometer smoke particles.
NAp Not applicable.
[1]1-g sample.

Table 3.—Toxic load data for chlorine-containing materials at 1,000 °C set furnace temperature

Material[1]	HCl, mg/g			CO, mg/g		Combined,[4] mg/g	CO_2, mg/g	Mass of particulates, mg/g	n_o,[5] 10^9 p/g	d_g,[6] μm
	Aerosol	Gaseous	Total[2]	Total	Normalized[3]					
P1	2.6	15.7	18.3	78	5.2	23.5	373.4	8.53	3	0.05
N1	1.4	15.23	16.63	59	3.93	20.56	294.5	4.73	2	0.01
S1	0.01	0.06	0.07	44	2.93	3	629	8.16	2	0.02
B1	0.02	33.4	33.42	90	6.0	39.42	334.1	3.7	7	0.09
F1	0.01	4	4.01	12	0.8	4.81	118	0.03	0.01	0.29

d_g Average diameter of submicrometer smoke particles.
n_o Average concentration of submicrometer smoke particles.
[1]1-g sample.
[2]Contains aerosol and gaseous loads.
[3]Carbon monoxide load values normalized to HCl values; each CO value has been divided by a factor of 15 because CO is at least 15 times less toxic than HCl.
[4]Contains total HCl and normalized CO loads.
[5]The n_o load values are the sum of n_o multiplied by a factor of 6.25 because the total airflow through the furnace is 6.25 times greater than the airflow through the SPDA.
[6]The d_g average size values are the sum of the d_g values divided by the experimental time.

By contrast, the lowest HCl concentrations, yielding the lowest HCl loads, were released by the S1 sample, followed by the F1 sample. This is attributed to the low content of chlorinated additives in the materials. The S1 sample, however, released the highest CO_2 concentrations and loads, and high concentrations and loads of CO. The CO load value, normalized to and combined with the HCl load value, increased the toxicity of the S1 material. Also, the S1 sample released high concentrations of submicrometer smoke particles and mass of particulates. On the other hand, the F1 sample released extremely small concentrations of CO and CO_2, small concentrations of submicrometer smoke particles (with the largest diameter), and mass of particulates.

Equation 1 may be used to predict the mass loss rates in a given ventilated system necessary to produce 100 ppm of HCl. Rearranging equation 1, equation 4 is derived:

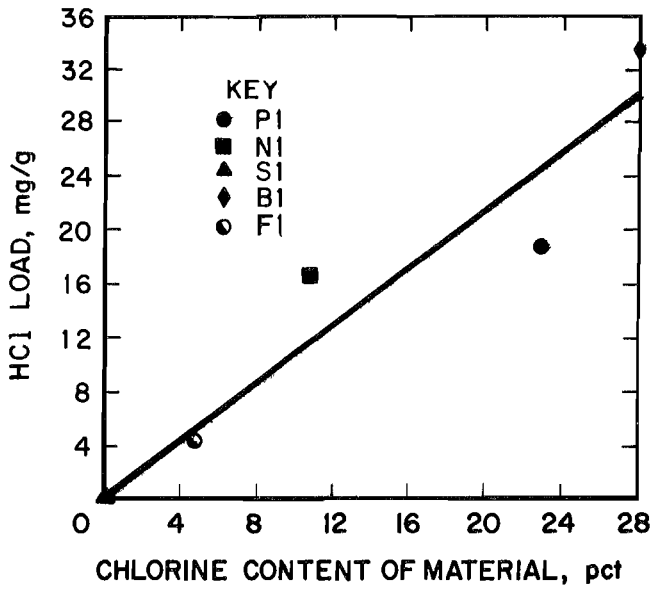
$$\dot{M}_s = \frac{(100) \times (Q) \times (C_{HCl})}{Y_{HCl}}. \quad (4)$$

Substituting equation 3 into equation 4 for Y_{HCl} (grams per gram), equation 5 is derived:

$$\dot{M}_s = \frac{(100) \times (Q) \times (C_{HCl})}{0.001054 \times Cl_2\ (pct) + 0.000315}. \quad (5)$$

As shown in figure 5 for the B1 sample (Cl_2 = 28 pct, as reported in table 1), the mass which needs to burn in a ventilated system with 4.7 m^3/s of airflow to produce 100 ppm of HCl is 26 g/s.

Figure 3



Hydrogen chloride load versus chlorine content of materials at 1,000 °C set furnace temperature.

NITROGEN-CONTAINING MATERIALS

All the samples underwent complete thermal decomposition (table 4); only friable ash-like residues remained. The Pr, Pn, and Ny samples, however, decomposed much more rapidly (dripping flaming droplets). The Wl sample, followed by the Ny, Pr, and Pn samples, released the highest HCN concentrations (mostly in the gaseous form) and yielded the highest HCN loads (table 5) because of the high nitrogen content of the materials. The HCN load values were correlated with the percentage of nitrogen contained in the materials using a least squares regression analysis (figure 6).

The fit, reported in equation 6, was found to be:

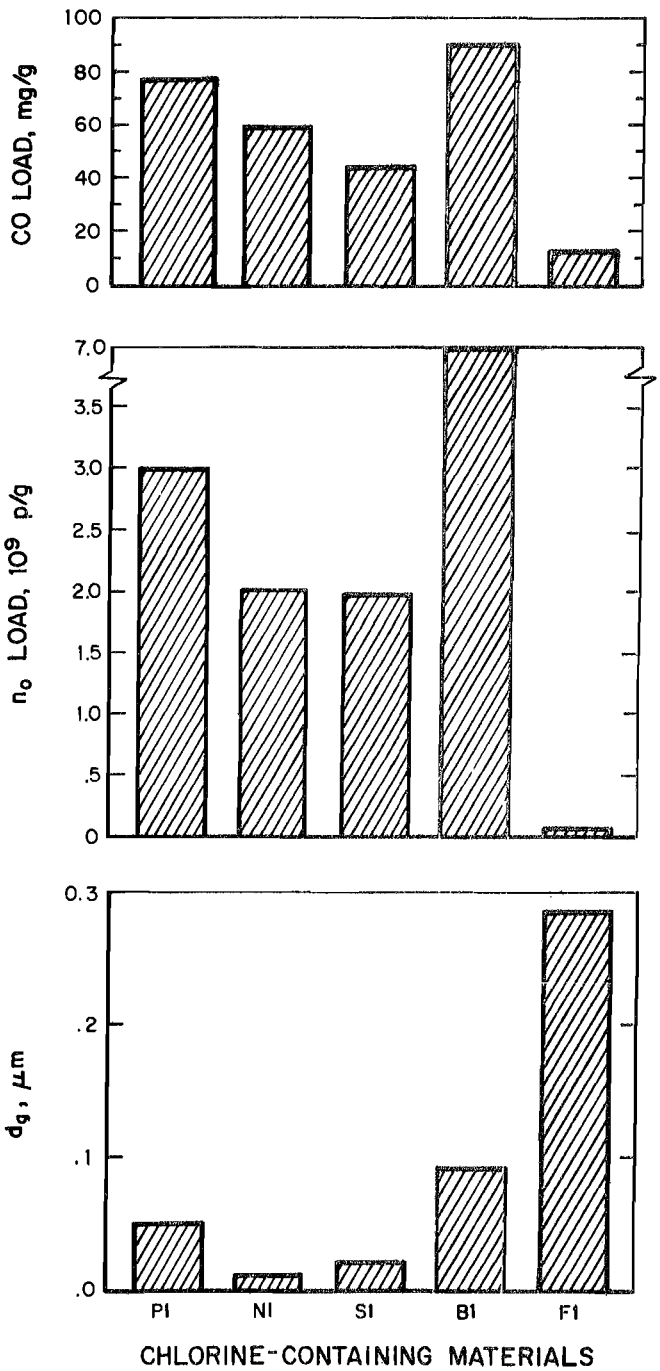
$$Y_{HCN}\ (g/g) = 0.000131 \times N\ (pct) + 0.000127. \quad (6)$$

The correlation coefficient (r^2) = 0.89; the standard deviation = 1.02.

The data indicate that a direct and significant relationship exists between the two parameters. The higher the nitrogen content, the higher the HCN value.

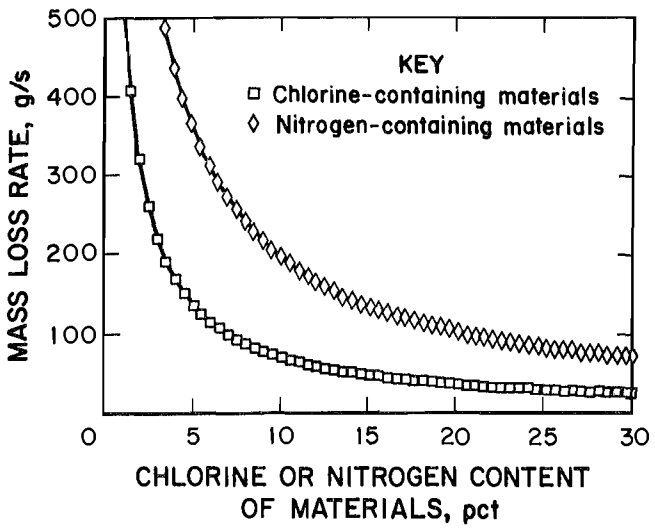
Also, Pr and Pn samples released very high concentrations and loads of CO and CO_2, submicrometer smoke particles (with a very small diameter), and mass of particulates (tables 4 and 5, and figure 7). The CO load

Figure 4



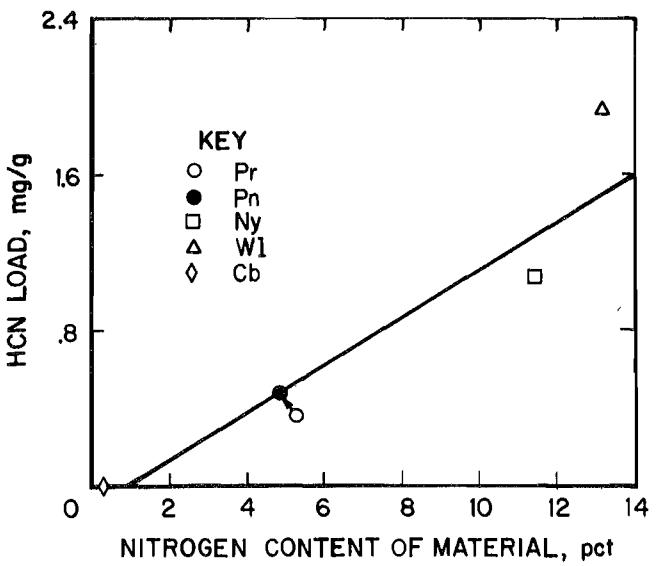
Carbon monoxide and average submicrometer smoke particle concentration loads, and particles' average diameter size for chlorine-containing materials at 1,000 °C set furnace temperature. (d_g = average diameter of submicrometer smoke particles; n_o = average concentration of submicrometer smoke particles.)

Figure 5



Mass loss rates to produce 100 ppm of HCl or 50 ppm of HCN (IDLH values) in a ventilated system (4.7 m^3/s) for chlorine- or nitrogen-containing materials.

Figure 6

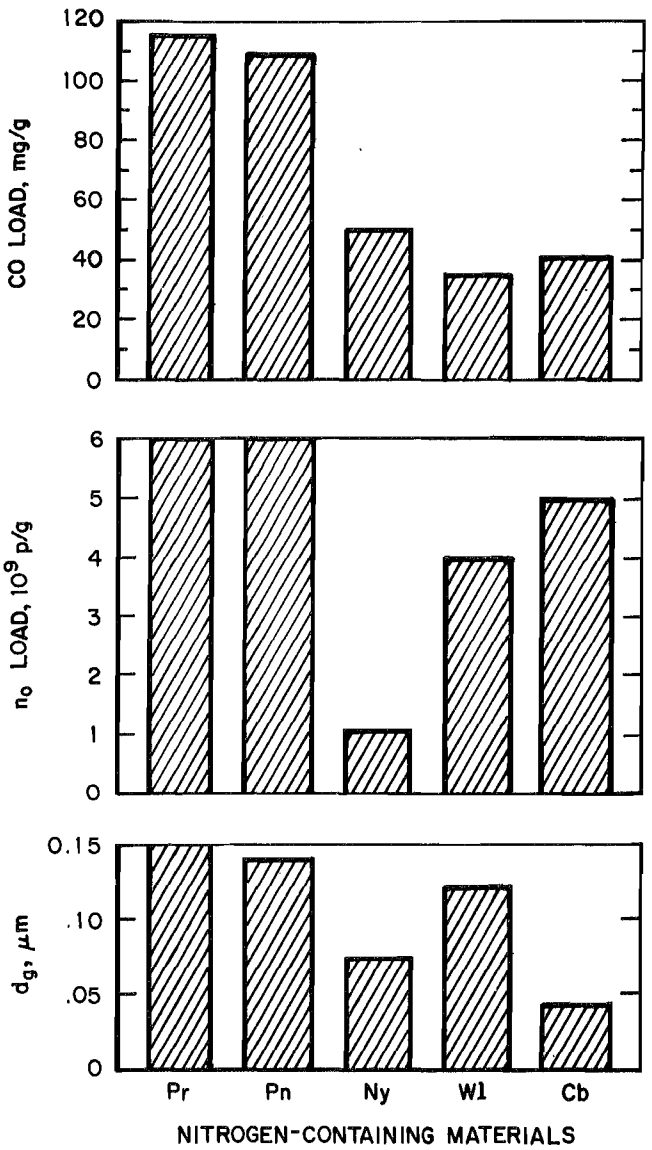


Hydrogen cyanide load versus nitrogen content of materials at 1,000 °C set furnace temperature.

values, normalized to and combined with the HCN load values, increased significantly the toxicity of these samples (table 5).

By contrast, the lowest HCN concentration, yielding the lowest HCN load, was released by the Cb sample. This was expected, based on the low nitrogen content of the material. This material also released modest

Figure 7



Carbon monoxide and average submicrometer smoke particle concentration loads, and particles' average diameter for nitrogen-containing materials at 1,000 °C set furnace temperature. (d_g = average diameter of submicrometer smoke particles; n_o = average concentration of submicrometer smoke particles.)

concentrations and loads of CO and CO_2, submicrometer smoke particles, and mass of particulates. Equation 2 may be used to predict the mass loss rates in a given ventilated system necessary to produce 50 ppm of HCN. Rearranging equation 2, equation 7 is derived:

$$\dot{M}_s = \frac{(50) \times (Q) \times (C_{HCN})}{Y_{HCN}}. \qquad (7)$$

Table 4.—Oxidative thermal decomposition data for nitrogen-containing materials at 1,000 °C set furnace temperature

Material[1]	Time, min	CO, ppm	CO_2, ppm	Temp, °C		n_o, 10^6 p/cm^3	d_g, μm	Total weight loss, g
				Sample	Furnace			
Pr	6	12	600	139	162	0	NAp	
	7	16	700	184	207	0	NAp	
	8	28	700	230	250	0	NAp	
	9	129	1,000	278	292	2	0.40	
	10	466	1,200	316	332	17	0.10	
	11	1,511	1,700	331	370	212	0.02	
	12	2,070	2,200	369	407	668	0.01	0.98
	13	1,820	2,600	441	446	108	0.90	
	14	906	2,600	535	482	1	0.30	
	15	717	1,900	538	509	8	0.01	
	16	318	1,800	549	537	8	0.01	
	17	284	1,900	577	570	2	0.14	
	18	242	2,100	611	597	3	0.11	
	19	150	1,500	600	605	2	0.10	
	20	100	800	587	619	1	0.10	
Pn	6	9	600	139	162	0	NAp	
	7	15	500	180	210	0	NAp	
	8	25	500	225	256	0	NAp	
	9	73	600	270	296	2	0.30	
	10	333	1,000	310	337	18	0.10	
	11	931	1,500	365	374	220	0.01	
	12	2,220	2,300	360	409	650	0.01	0.98
	13	2,250	2,000	445	441	100	0.90	
	14	933	2,200	530	474	2	0.26	
	15	760	1,100	539	504	6	0.01	
	16	384	1,300	550	534	7	0.01	
	17	284	1,900	570	569	1	0.14	
	18	242	2,000	610	590	2	0.10	
	19	145	1,300	600	600	1	0.10	
	20	90	700	585	620	1	0.10	
Ny	6	10	500	99.5	158	0	NAp	
	7	15	500	137	203	4	<0.01	
	8	25	500	176	247	3	0.05	
	9	32	500	216	288	2	0.18	
	10	62	600	237	327	1	0.22	
	11	364	800	267	364	5	0.04	
	12	1,600	1,400	313	402	4	0.11	0.99
	13	2,200	2,100	376	436	21	0.04	
	14	1,700	2,400	468	470	56	0.03	
	15	1,150	2,500	520	502	67	0.02	
	16	507	2,000	575	532	12	0.07	
	17	383	2,100	620	560	4	0.10	
	18	293	2,000	645	587	3	0.10	
	19	190	1,300	620	600	2	0.10	
	20	99	800	600	619	1	0.10	
WI	6	10	500	105	157	0	NAp	
	7	20	500	141	203	0	NAp	
	8	52	500	186	246	0	NAp	
	9	66	600	237	288	0.08	0.81	
	10	119	700	270	328	1	0.26	
	11	212	1,000	312	367	29	0.05	
	12	415	1,600	345	402	182	0.01	0.97
	13	540	1,700	386	437	156	0.01	
	14	695	2,000	432	473	149	0.01	
	15	554	2,100	474	503	40	0.04	
	16	396	2,000	512	533	4	0.12	
	17	243	1,900	550	561	3	0.12	
	18	185	1,900	590	589	3	0.11	
	19	100	1,000	550	600	2	0.10	
	20	75	700	540	620	1	0.10	

See explanatory notes at end of table.

Table 4—Oxidative thermal decomposition data for nitrogen-containing materials at 1,000 °C set furnace temperature—Continued

Material[1]	Time, min	CO, ppm	CO_2, ppm	Temp, °C		n_o, 10^6 p/cm^3	d_g, μm	Total weight loss, g
				Sample	Furnace			
Cb	6	10	500	142	162	0.23	0.28	
	7	15	500	186	208	2	0.02	
	8	28	700	233	251	5	0.04	
	9	48	600	279	293	22	0.04	
	10	80	700	324	332	41	0.03	
	11	151	800	380	369	129	0.02	
	12	611	1,400	450	406	133	0.01	0.86
	13	499	1,300	485	440	113	0.02	
	14	424	1,400	514	471	89	0.02	
	15	478	1,700	547	502	66	0.02	
	16	558	2,000	574	533	56	0.02	
	17	499	2,200	595	561	56	0.02	
	18	316	1,600	624	589	49	0.03	
	19	210	1,000	600	600	29	0.02	
	20	150	700	590	620	10	0.01	

d_g Average diameter of submicrometer smoke particles.
n_o Average concentration of submicrometer smoke particles.
NAp Not applicable.
[1]1-g sample.

Table 5.—Toxic load data for nitrogen-containing materials at 1,000 °C set furnace temperature

Material[1]	HCN, mg/g			CO, mg/g		Combined,[4] mg/g	CO_2, mg/g	Mass of particulates, mg/g	n_o,[5] 10^9 p/g	d_g,[6] μm
	Aerosol	Gaseous	Total[2]	Total	Normalized[3]					
Pr	0.0005	0.425	0.426	115.4	3.85	4.28	354	5.3	6	0.15
Pn	0.005	0.420	0.425	110.0	3.67	4.11	432.3	5	6	0.14
Ny	0.007	1.125	1.132	52.4	1.75	2.88	216.2	5.6	1	0.07
Wl	0.018	1.85	1.87	36.6	1.22	3.10	275.1	6.9	4	0.12
Cb	0.002	0.03	0.032	43.3	1.44	1.47	235.8	3	5	0.04

d_g Average diameter of submicrometer smoke particles.
n_o Average concentration of submicrometer smoke particles.
[1]1-g sample.
[2]Contains aerosol and gaseous loads.
[3]Carbon monoxide load values normalized to HCN values; each CO value has been divided by a factor of 15 because CO is at least 15 times less toxic than HCN.
[4]Contains total HCN and normalized CO loads.
[5]The n_o load values are the sum of n_o multiplied by a factor of 6.25 because the total airflow through the furnace is 6.25 times greater than the airflow through the SPDA.
[6]The d_g average size values are the sum of the d_g values divided by the experimental time.

Substituting equation 6 into equation 7 for Y_{HCN} (grams per gram) equation 8 is derived:

$$\dot{M}_s = \frac{(50) \times (Q)\ (C_{HCN})}{0.00131 \times N\ (pct) \times 0.000127}. \qquad (8)$$

As shown in figure 5 for the Wl sample (N = 13.25 pct, as reported in table 1), the mass which needs to burn in a ventilated system with 4.7 m^3/s of airflow to produce 50 ppm of HCN is 152.8 g/s. Also, figure 5 illustrates the potential use of the HCl and HCN correlations with the chlorine and nitrogen contents, respectively (equations 5 and 8). The two curves represent the mass-loss rates of samples necessary to produce the toxic hazard (IDLH value) as a function of the chlorine or nitrogen percentages in the original materials. The calculation assumes an airflow of 4.7 m^3/s. At higher airflows, higher mass-loss rates would be required, while at lower airflows, lower mass-loss rates would be required to produce the same toxic levels of either HCl or HCN. What is important to note is that as the chlorine or nitrogen contents of the material increase, the mass-loss rates decrease markedly. This means that a relatively small sample could produce a high toxicity if the chlorine or nitrogen contents are high.

CONCLUSIONS

According to these findings, the HCl and HCN concentrations (treated as load values), evolved during the combustion of chlorine- and nitrogen-containing materials, correlate directly and significantly with the chlorine and nitrogen contents of the respective materials. The higher the percentage of chemical contents, the higher the gas concentrations.

In the case of the chlorine-containing materials, all the samples (except F1, which contains 90 pct glass fiber) underwent complete thermal decomposition; only ash-like residues remained. The B1 and P1 samples, followed by the N1 sample, released the highest HCl concentrations (mostly in the gaseous form) and yielded the highest HCl loads because of the high chlorine content of the materials. Also, these materials released high concentrations and loads of CO, which significantly increased their toxicity. Large concentrations of submicrometer smoke particles (on whose surface HCl droplets attach) and mass of particulates were also released by these materials. The F1 material released much smaller concentrations of HCl, CO, submicrometer smoke particles, and mass of particulates and may be considered less hazardous during a fire. The S1 sample may be considered toxicologically less hazardous during fire, according to the comparison between its combined load value and similar values reported for the P1 and N1 samples; however, the rates at which the toxic load is released may make this material more hazardous than the other materials tested.

In the case of the nitrogen-containing materials, all the samples underwent complete thermal decomposition; only ash-like residues remained. The Wl sample, followed by the Ny, Pr, and Pn samples, released the highest HCN concentrations (mostly in the gaseous form) and yielded the highest HCN loads because of the high nitrogen content of the materials.

However, the Pr, Pn, and Ny samples decomposed much more rapidly (dripping flaming droplets). Furthermore, the Pr and Pn samples released extremely high concentrations and loads of CO, which significantly increased the toxicity of these materials. Large concentrations of submicrometer smoke particles and mass of particulates were also released by these materials.

In summary, the correlations developed in this study indicate that it is possible to determine the primary toxic gas load values (HCl and HCN) for these two classes of materials, simply and inexpensively. It follows that the materials, organized in classes, may be ranked according to various factors, such as the percentage of the chemical contents in the original sample, the primary and the combined toxic load values evolved during the combustion of the materials, and the mass of material that needs to burn to yield IDLH values in a ventilated system.

Finally, the ranking of all these factors may help mine safety personnel to differentiate among mine materials before the materials are brought in the mines.

REFERENCES

1. Fowell, A. J. Assessing Toxic Hazard as It Relates to Overall Fire Hazard. Fire Tech., v. 21, No. 3, Aug. 1985, pp. 199-212.

2. Snell, T. E., B. C. Levin, and A. J. Fowell. Workshop on Combustion Product Toxicity. Natl. Bur. Stand. Tech., Cent. Fire Res., Washington, DC, NBSIR 822634, Sept. 10, 1982, pp. 1-65.

3. International Labor Office (Geneva). Encyclopedia of Occupational Health and Safety. V. 21, 1983, p. 1085.

4. ____. Encyclopedia of Occupational Health and Safety. V. 1, 1983, p. vi.

5. Barrow, C. S., H. Lucia, and Y. C. Alarie. A Comparison of the Acute Inhalation Toxicity of Hydrogen Chloride Versus the Thermal Decomposition Products of Polyvinyl Chloride. J. Combust. Toxicol., v. 6, Feb. 1979, pp. 3-11.

6. Barrow, C. S., Y. C. Alarie, J. C. Warrick, and M. F. Stock. Comparison of the Sensory Irritation Response in Mice to Chlorine and Hydrogen Chloride. Arch. Environ. Health, v. 32, Mar.-Apr. 1977, pp. 68-75.

7. Burleigh, A., H. Flayer, K. L. Wona, and Y. C. Alarie. Evaluation of the Pulmonary Effects of HCl Using CO_2 Challenges in Guinea Pigs. Fundam. Appl. Toxicol., v. 5, 1985, pp. 978-985.

8. Malek, D. E., M. F. Stock, and Y. C. Alarie. Performance Evaluation Under Intoxicating Atmospheres. Fundam. Appl. Toxicol., v. 8, 1987, pp. 335-345.

9. Levin, B. C., M. Paabo, J. L. Gurman, and S. E. Harris. Toxicity of Mixed Gases Found in Fires. Paper in Progress in Fire Safety Technology—Research Activities—Codes and Regulations—Hazard Assessment. (Joint Meet. Soc. Plast. Ind., Inc., and Fire Retard. Chem. Assoc.). Technomic Publ., Lancaster, PA, 1986, pp. 71-88.

10. International Labor Office (Geneva). Encyclopedia of Occupational Health and Safety. V. 1, 1983, pp. 574-577.

11. Alarie, Y. C., E. Wilson, T. Civic, J. H. Magill, T. M. Funt, C. S. Barrow, and J. Frohlinger. Sensory Irritation Evoked by Polyurethane Decomposition Products. J. Combust. Toxicol., v. 2, May 1975, pp. 139-149.

12. Caldwell, D. J., and Y. C. Alarie. A Method To Determine the Potential Toxicity of Smoke From Burning Polymers. J. Fire Sci., v. 9, Nov. 1991, pp. 470-518.

13. Matisak-Schaper, M., and Y. C. Alarie. Toxicity of Carbon Monoxide, Hydrogen Cyanide and Low Oxygen. J. Combust. Toxicol., v. 9, Feb. 1982, pp. 21-60.

14. Lieu, P. J., J. H. Magill, and Y. C. Alarie. Flammability-Toxicity Ratings of Some Polyphosphazene and Polyurethane Foams. J. Combust. Toxicol., v. 8, Nov. 1987, pp. 242-259.

15. Esposito, F. M., and Y. C. Alarie. Inhalation Toxicity of Carbon Monoxide and Hydrogen Cyanide Gases Released During the Thermal Decomposition of Polymers. J. Fire Sci., v. 6, May-June 1988, pp. 195-242.

16. Levin, B. C., J. L. Gurman, M. Paabo, L. Baier, and T. Holt. Toxicological Effects of Different Time Exposures to the Fire Gases: Carbon Monoxide or Hydrogen Cyanide or to Carbon Monoxide Combined With Hydrogen Cyanide or Carbon Dioxide. Natl. Bur. Stand., Gaithersburg, MD, NBSIR 88-3753, 1988, 88 pp.

17. International Labor Office (Geneva). Encyclopedia of Occupational Health and Safety. V. 1, 1983, pp. 395-399.

18. Hartzell, G. E., D. N. Priest, and W. G. Switzer. Mathematical Modeling of Toxicological Effects of Fire Gases. Paper in Fire Safety

Science Proceedings of the First International Symposium (Int. Assoc. Fire Saf. Sci., Gaithersburg, MD, Oct. 7-11, 1985). Hemisphere Publ., Sept. 1986, pp. 1059-1068.

19. Pitts, W. M. Carbon Monoxide Production and Prediction. Paper in 11th Joint Panel Meeting of the UJNR Panel on Fire Research and Safety. Natl. Inst. Stand. Tech., Gaithersburg, MD, NISTIR 4449, 366 pp. 1989, pp. 33-39.

20. Stewart, D. R. The Effect of Carbon Monoxide on Man. Smoke and Products of Combustion. Technomic Publ., Fire Flammability Ser., v. 15, p. 2, 1976, pp. 371-379.

21. Coffin, D. L., and H. E. Stokinger. Biological Effects of Air Pollutants in Air Pollution. Acad. Press, New York, 3rd ed., v. 2, 1977, pp. 231-360.

22. De Rosa, M. I., and C. D. Litton. Oxidative Thermal Degradation of PVC-Derived, Fiberglass, Cotton, and Jute Brattices, and Other Mine Materials. A Comparison of Toxic Gas and Liquid Concentrations and Smoke-Particle Characterization. USBM RI 9058, 1986, 13 pp.

23. ____. Determining the Relative Toxicity and Smoke Obscuration of Combustion Products of Mine Combustibles. USBM RI 9274, 1989, 11 pp.

24. ____. Primary Gas Toxicities and Smoke Particle Characteristics During Combustion of Mine Ventilation Ducts. Development of a Test Parameter. USBM RI 9284, 1989, 11 pp.

25. ____. Utilization of Smoke Properties for Predicting Smoke Toxicity. Paper in Recent Developments in Metal and Nonmetal Mine Fire Protection. USBM IC 9206, 1988, pp. 72-77.

26. ____. Primary Gas Toxicities and Smoke Particle Characteristics During a Two-Stage Combustion of Mine Conveyor Belts. Development of a Test Parameter. USBM RI 9250, 1989, 13 pp.

27. ____. Primary Gas Toxicities and Smoke Particle Characteristics During Combustion of Mine Brattices. Development of a Test Parameter. USBM RI 9262, 1989, 13 pp.

28. ____. Embedded Hydrogen Chloride and Smoke Particle Characteristics During Combustion of Polyvinyl Chloride and Chlorinated Mine Materials. USBM RI 9368, 1991, 13 pp.

29. De Rosa, M. I., and C. D. Litton. Hydrogen Cyanide and Smoke Particle Characteristics During Combustion of Polyurethane Foams and Other Nitrogen-Containing Materials. Development of a Test Parameter. USBM RI 9367, 1991, 15 pp.

30. Levin, B. C., M. Paabo, L. Highbarger, and N. Eller. Synergistic Effects of Nitrogen Dioxide and Carbon Dioxide Following Acute Inhalation Exposures in Rats. Natl. Inst. Stand. Tech., Gaithersburg, MD, NISTIR 89-4105, May 1989, pp. 1-37.

31. Stone, J. P., R. N. Hazlett, J. E. Johnson, and H. W. Carhart. The Transport of Hydrogen Chloride by Soot From Burning Polyvinyl Chloride. Smoke and Products of Combustion. Technomic Publ., Fire Flammability Ser., v. 2, 1961, pp. 135-144.

32. Weckman, E. J., and C. Salvador. Additive Effects on Soot Formation in Laboratory Pool Fires. Paper in Abstracts: Annual Conference on Fire Research (Rockville, MD, Oct. 13-15, 1992). Natl. Inst. Stand. Tech., Gaithersburg, MD, NISTIR 4924, 1992, pp. 65-66.

33. Thomas, D. M., and E. H. Connor. Management of the Patient Overcome by Smoke. J. KY Med. Assoc., v. 66, 1968, p. 1051.

34. Alarie, Y. C. The Toxicity of Smoke From Polymeric Materials During Thermal Decomposition. Ann. Rev. Pharmacol. Toxicol., v. 25, 1985, pp. 325-347.

35. Hygget, C., and B. C. Levin. Toxicity of the Pyrolysis of Combustion Products of Polyvinyl Chlorides: A Literature Review. Fires Mater., v. 11, 1987, pp. 131-142.

36. Boettner, E. A. Combustion of Products From Incineration of Plastics. Univ. MI, Div. Res. Dev., Ann Arbor, MI, EPA contract 032050, Feb. 1973, 200 pp.

37. Kaplan, H. L., A. F. Grand, and G. E. Hartzell. Combustion Toxicology Principles and Test Methods. Technomic Publ., Lancaster, PA, 1983, pp. 1-167.

38. Litton, C. D., and M. Hertzberg. Principles of Ionization Smoke Detection. Development of a New Sensor for Combustion-Generated Submicrometer Particulates. USBM RI 8242, 1977, 21 pp.